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Performance of cryogenic thermoelectric generators in LNG cold energy utilization

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Abstract

The cold energy of liquefied natural gas (LNG) is generally wasted when the LNG is extracted for utilization. This paper proposes cryogenic thermoelectric generators to recover this cold energy. The theoretical performance of the generator has been analyzed. An analytical method and numerical method of calculation of the optimum parameters of the generator have been demonstrated.

Keywords: Thermoelectric generators; Cold energy

1. Introduction

Thermoelectric generators are driven by large temperature differences to convert the heat flow through them into electric power output. Because of their relatively low conversion efficiency, their applications are usually limited to specific situations where their simple, reliable and compact characteristics present advantages. However, one exception is the thermoelectric recovery of waste heat or cold when the large temperature difference can be provided without consideration of cost. Consequently, the low conversion efficiency is not a serious drawback. Natural gas is known as a clean energy source commonly used as a domestic and industrial fuel

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for combustion. It is liquefied to transport and stored at atmospheric pressure and at a temperature of about −162 °C. When supplied for utilization, the liquefied natural gas (LNG) should be vaporized. Its latent heat of vaporization and any sensible heat required to superheat the vapour are termed 'cold energy', which is generally supplied by sea water. Cold energy is a high quality energy source from the point view of thermodynamics [1]. If thermoelectric generators are operated during the vaporization and temperature increasing processes of the LNG, with the two ends of the generator's arms maintained at the sea water temperature and the LNG temperature, respectively, then the cold energy flow though the arms can be partly converted into electrical power output. Previous investigations [2–5] of thermoelectric generators have been focused on converting waste heat, which has a different energy source and operation temperature range from that for converting LNG cold energy. For thermoelectric recovery of the LNG cold energy, the energy source is the heat sink with temperature well below ambient temperature, which provides the cold energy, namely, absorbs heat from the ambient environment. The important design parameters of the power generators are the efficiency, power output and the optimal size and load resistance. In the present paper, we firstly give the analytic solutions with constant transport coefficients and compare them with those of thermoelectric generators converting waste heat. Then, we employ a numerical method with real temperature dependent material parameters. The calculation results of the two methods are compared and analyzed to give a profile of the optimal design and performance of thermoelectric generators converting LNG cold energy to electric power output.

2. Maximum efficiency and power output

According to the fundamental theory of thermoelectricity [6], when an electric current density $\vec{j}$ exists in addition to a temperature gradient $\nabla_{\vec{r}}T$ in the semiconductor sample, the heat flow density ($\vec{q}$) and the heat generated per unit time ($\dot{q}$) are given by:

$$\vec{q} = \vec{j}TS - k\nabla_{\vec{r}}T \tag{1}$$

$$\dot{q} = j^2\rho - \tau(\vec{j}\cdot\nabla_{\vec{r}}T) + \nabla_{\vec{r}}(k\nabla_{\vec{r}}T) \tag{2}$$

where S is the Seebeck coefficient, k the thermal conductivity, ρ the electric resistivity, and τ the Thomson coefficient, which is provided by the first Kelvin relation with Seebeck coefficient as:

$$\tau = T\frac{\mathrm{d}S}{\mathrm{d}T} \tag{3}$$

The second term in Eq. (2) is the Thomson heat, while the first and third terms are the Joule heat and heat transport by thermal conduction, respectively.

For a standard thermoelectric generator as shown in Fig. 1, one end of its arms remains at the temperature T_{h} of the heat source, while the other end remains at the temperature T_{c} of the heat sink. The current is assumed to flow in one dimension, as along the arm of the generator. We assume steady state. Therefore, in an n-type arm, Eqs. (1) and (2) are presented as:

$$q(x) = jT(x)S(x) - k(x)\frac{\mathrm{d}T}{\mathrm{d}x} \tag{4}$$

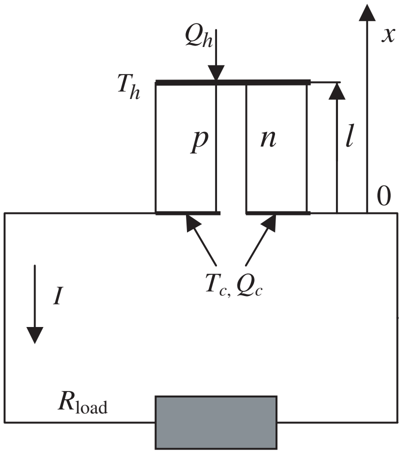

Fig. 1. Schematic diagram of a thermoelectric generator.

$$j^2\rho(x) - T\frac{\mathrm{d}S(x)}{\mathrm{d}x}j + \frac{\mathrm{d}}{\mathrm{d}x}\left(k(x)\frac{\mathrm{d}T(x)}{\mathrm{d}x}\right) = 0 \tag{5}$$

As in the p-type arm, there exist similar equations, in which the only difference is that the electrical current flows in the opposite direction of that in the n arm, so

$$I = j_{\mathrm{n}}A_{\mathrm{n}} = -j_{\mathrm{p}}A_{\mathrm{p}} \tag{6}$$

where $A_{\mathrm{n}}, A_{\mathrm{p}}$ are the cross-sectional areas of the n arm and p arm, respectively.

For calculation simplicity, the material parameters (S, ρ, k) are taken as constants, or if they depend upon temperature, the values are taken at the mean temperature of the materials. With these approximations, the solutions to Eqs. (4) and (5) are:

$$T(x) = T_{\mathrm{c}} + \frac{x}{l}\Delta T + \frac{\rho j^2}{2k}x(l-x) \tag{7}$$

$$q(x) = jST(x) - k\frac{\Delta T}{l} - \frac{1}{2}\rho j^2(l-2x) \tag{8}$$

where $\Delta T = T_{\mathrm{h}} - T_{\mathrm{c}}$, and l is the length of the arms.

The temperature distribution along the arm of the device is given by Eq. (7). We can then obtain the heat flow density at each end of the device $q_{x=0}$ and $q_{x=l}$ by Eq. (8). From the energy balance, we find that the power output of the generator equals the difference between the heat absorbed from the hot side and the heat supplied to the cold side. In using the LNG cold energy to generate electrical power, the efficiency of the generator η is defined as the power output divided by the heat supplied to the cold reservoir.

$$\eta = \frac{q_{\mathrm{n},x=l}A_{\mathrm{n}} + q_{\mathrm{p},x=l}A_{\mathrm{p}} - q_{\mathrm{n},x=0}A_{\mathrm{n}} - q_{\mathrm{p},x=0}A_{\mathrm{p}}}{q_{\mathrm{n},x=0}A_{\mathrm{n}} + q_{\mathrm{p},x=0}A_{\mathrm{p}}} = \frac{q_{\mathrm{n},x=l} + q_{\mathrm{p},x=l}\beta - q_{\mathrm{n},x=0} - q_{\mathrm{p},x=0}\beta}{q_{\mathrm{n},x=0} + q_{\mathrm{p},x=0}\beta} \tag{9}$$

where $\beta = A_{\mathrm{p}}/A_{\mathrm{n}}$.

Combined with Eqs. (6)–(8), Eq. (9) gives the efficiency of the device for given I and β. From $\frac{\partial\eta}{\partial I} = 0$ and $\frac{\partial\eta}{\partial\beta} = 0$, η can be maximized as:

$$\eta_{\max} = \frac{\Delta T(1 - 1/\varepsilon)}{T_c + T_h/\varepsilon} \tag{10}$$

when

$$I_\eta = \frac{\Delta S\,\Delta T}{r(\varepsilon + 1)} \tag{11}$$

and

$$\beta = \sqrt{\frac{k_n\rho_p}{k_p\rho_n}} \tag{12}$$

where $\Delta S = S_p - S_n$ (S_p is the Seebeck coefficient of the p-type material, and S_n is the Seebeck coefficient of the n-type material in the device), r is the internal electrical resistance of the device, which is defined as $r = (\rho_n/A_n + \rho_p/A_p)l$.

$$\varepsilon = \sqrt{1 + ZT_m} \tag{13}$$

where $T_m = (T_h + T_c)/2$ is the mean temperature, the figure of merit $Z = \frac{\Delta S^2}{Kr}$, and K is the thermal conductance of the device, defined as

$$K = k_n\frac{A_n}{l} + k_p\frac{A_p}{l}$$

To have $\eta_{\max}$, the outside load resistance should be

$$R_{load} = \frac{\Delta S\,\Delta T}{I_\eta} - r = \varepsilon r \tag{14}$$

The maximizing values β in Eq. (12) and R_{load} in Eq. (14) are identical to those for waste heat conversion generators [3]. However, the maximum efficiency for the later is $\eta_{\max,heat} = \frac{\Delta T(1-1/\varepsilon)}{T_h+T_c/\varepsilon}$. Comparing with Eq. (10) indicates that the efficiency for converting LNG cold energy should be larger than that for converting waste heat, which is reasonable because cold energy is a higher quality energy source than heat from the point of view of thermodynamics. Fig. 2 shows the maximum conversion efficiency of these two types of generators. We can also deduce from Eq. (10) that if the dimensionless figure of merit ZT_m dose not change much, the device should have better performance between larger temperature differences ΔT and in a lower temperature region since the efficiency increases with the decrease of T_h and T_c. As $\varepsilon \to \infty$ the efficiency approaches the Carnot efficiency.

The electrical power output is given by:

$$P = I(\Delta S \cdot \Delta T - Ir) \tag{15}$$

At the maximum efficiency, I can be eliminated by Eq. (11), and by replacing r by its definition, Eq. (15) yields:

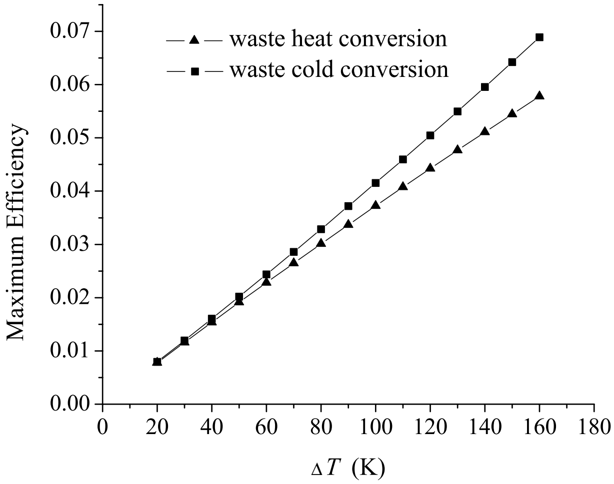

Fig. 2. Maximum efficiency of thermoelectric generators vs. temperature difference ΔT. T_c for waste heat conversion and T_h for LNG cold energy conversion are the ambient temperature of 290 K. The figure of merit Z is assumed as 0.002 K^{-1}.

$$P_\eta = \left(\frac{\Delta S\,\Delta T}{\varepsilon+1}\right)^2 \frac{\varepsilon}{r} = \frac{A_n}{l}\left(\frac{\Delta S\,\Delta T}{\varepsilon+1}\right)^2 \frac{\varepsilon}{(\rho_n+\rho_p/\beta)} \tag{16}$$

The power output of the device is proportional to the ratio of the cross-sectional area to the length of the thermoelement, which suggests that the shorter the thermoelectric arm the larger will be the power output per unit area, consistent with what is shown in Fig. 3 in Ref. [4] by measuring several thermoelectric modules of different sizes. However, for real thermoelectric generators, this is not always the case because of the unavoidable thermal resistance between the arms and the heat reservoirs caused by the conducting strips between the arms and the electrical insulating layer at each end in addition to the contact resistance. After the length decreases to a certain value, if the arms become shorter, then the temperature difference will largely occur on these thermal resistances rather on the arms, and thus, the power output will consequently decrease sharply.

3. Numerical approach with temperature dependent material properties

When thermoelectric generators convert LNG cold energy to electric power output, the working temperatures usually range from ambient temperature to below ambient by more than −150 °C, and the material parameters vary with temperature largely in this temperature region according to experimental data [7,8]. Therefore, analysis of the performance of the device by assuming constant material parameters must bring in considerable deviation from the true values. Whenever the transport coefficients vary with temperature, numerical procedures must be used to solve Eqs. (4), (5) and (9) [5]. By algebraic manipulations, Eqs. (4) and (5) can be converted into:

$$\frac{dT}{dx} = [\bar{j}T(\bar{x})S(\bar{x}) - \bar{q}(\bar{x})]/k(\bar{x}) \tag{17}$$

$$\frac{d\bar{q}}{d\bar{x}} = \rho(\bar{x})\bar{j}^2[1 + Z(\bar{x})T(\bar{x})] - \frac{\bar{j}S(\bar{x})\bar{q}(\bar{x})}{k(\bar{x})} \tag{18}$$

where $\bar{x} = x/l$, $\bar{j} = jl$ and $\bar{q} = ql$. For a given $\bar{j}$, $T(\bar{x})$ and $\bar{q}(\bar{x})$ along the arm can be obtained from the above two recursion relations with the boundary conditions $T(\bar{x} = 0) = T_c$ and $T(\bar{x} = 1) = T_h$. The efficiency of the device can then be calculated by Eq. (9) as:

$$\eta = \frac{\bar{q}_{n,\bar{x}=1} + \bar{q}_{p,\bar{x}=1}\beta - \bar{q}_{n,\bar{x}=0} - \bar{q}_{p,\bar{x}=0}\beta}{\bar{q}_{n,\bar{x}=0} + \bar{q}_{p,\bar{x}=0}\beta} \tag{19}$$

Therefore, the maximum efficiency can be obtained by finding the optimal values of $\bar{j}$ and β.

The electric power output can be calculated by:

$$P_{\eta_{\max}} = (V_n + V_p)I - I^2 r = \frac{A_n}{l}\bar{j}_n\left[\int_0^1 d\bar{x}|S_n(\bar{x})|\frac{dT}{d\bar{x}} + \int_0^1 d\bar{x}|S_p(\bar{x})|\frac{dT}{d\bar{x}} - \bar{j}_n(\bar{r}_n + \bar{r}_p/\beta)\right] \tag{20}$$

where $\bar{r}_i = \int_0^1 d\bar{x}\rho_i(\bar{x})$, $i = n, p$.

4. Discussions

In bulk materials, Bi–Sb alloys as n-type and $CsBi_4Te_6$ as p-type material have been reported to have the highest figure of merit up to now at low temperature [9]. However, a complete TE device needs both a p-type and an n-type version of a material to operate. Thermoelectric modules composed of p-type $Bi_{0.5}Sb_{1.5}Te_3$ and n-type $Bi_2Te_{3-x}Se_x$ with $x = 0.12$–0.3 is a practical material for cold energy conversion thermoelectric generators. In the analytic method, the figure of merit Z of the material is assumed to be a constant, however, for real materials, it may vary greatly with decreasing temperature, dropping from 0.003 K^{-1} at 300 K to 0.0015 K^{-1} at 150 K [7]. We calculate the device parameters of a cryogenic thermoelectric generator by both the analytic method with the value of the material transport coefficients (S, ρ, k) at the mean temperature and the numerical method with these coefficients being temperature dependent. The device is composed of p-type Bi_2Te_3–Sb_2Te_3 alloy and n-type Bi_2Te_3–Bi_2Se_3 alloy with their transport coefficients polynomial fitted with $S(T)$, $1/\rho(T)$, $k(T)$ curves measured by Ref. [8] for No. 1 materials.

$$\begin{array}{ll}
S_p = -48.27 + 1.342T - 1.650 \times 10^{-3}T^2 & \mu V/K \\
S_n = -16.02 - 0.9636T + 1.120 \times 10^{-3}T^2 & \mu V/K \\
1/\rho_p = 1.314 \times 10^4 - 99.75T + 0.2925T^2 - 3.082 \times 10^{-4}T^3 & (\Omega\,cm)^{-1} \\
1/\rho_n = 1.154 \times 10^4 - 101.7T + 0.3502T^2 - 4.247 \times 10^{-4}T^3 & (\Omega\,cm)^{-1} \\
k_p = 73.07 - 0.6057T + 2.290 \times 10^{-3}T^2 - 3.068 \times 10^{-6}T^3 & mW/(cm\,K) \\
k_n = 45.05 - 0.2471T + 6.892 \times 10^{-4}T^2 - 6.752 \times 10^{-7}T^3 & mW/(cm\,K)
\end{array}$$

The calculations results are listed in Table 1. The operating temperature range is from $T_c = 130$ K to $T_h = 290$ K. The area A_n and the length of the device are 1 cm^2 and 1 cm, respectively.

It is quite interesting to note that although the material parameters change greatly with temperature, the analytic method using mean temperature values gives a very good approximation relative to the exact numerical solutions. From our calculations, we find that the material transport coefficients at the mean temperature are close to the average values for the operating

Table 1
Values of relevant parameters of the thermoelectric device adjusted to maximize the LNG cold energy conversion efficiency

	η_{max}	I (A)	Q_c (W)	R_{load}/r	β
Analytic method	0.096	20.88	6.43	1.273	0.84
Numerical solution	0.090	20.53	6.64	1.293	0.86

$T_c = 130$ K, $T_h = 290$ K, No.1 materials (p-type Bi_2Te_3–Sb_2Te_3 alloy and n-type Bi_2Te_3–Bi_2Se_3 alloy) in Ref. [8].

temperature range. Although thermoelectric materials have a variable stoichiometry, the transport coefficients may vary wildly with different fabrication processes. The temperature dependence of the transport coefficients of the No.1 materials in Ref. [8] is typical, and therefore, the values in Table 1 can give an estimate of the accuracy of the analytic method. Ref. [5] also shows that the analytic method represents a good approximation, although the material properties and temperature range are different from our case. It is good news for engineers that once the temperature range is determined, the optimal design values can be easily calculated with the materials transport coefficients at the mean temperature. The maximum efficiency given by the analytic method tends to be higher than the actual value. Nevertheless, the actual conversion efficiency can reach 9%, which is very good for thermoelectric generators with a temperature difference of only 160 K.

5. Conclusions

The performance of a LNG cold energy conversion thermoelectric generator has been investigated analytically and numerically. Results show that the efficiency of cold energy conversion is better than that of waste heat conversion, although the optimum parameters of A_p/A_n and external resistance R_{load} have the same calculation equations for these two kinds of energy sources. The calculation results indicate that the analytical method with material parameters evaluated at the mean temperature provides good accuracy for optimum parameters engineering design for LNG cold energy conversion generators.

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